



Degradation mechanism of diethyl phthalate with electrogenerated hydroxyl radical on a Pd/C gas-diffusion electrode

Hui Wang^{a,*}, De-Zhi Sun^a, Zhao-Yong Bian^{b,*}

^a College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, PR China

^b Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China

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ABSTRACT

Using a self-made Pd/C gas-diffusion electrode as the cathode and a Ti/IrO₂/RuO₂ anode, the degradation of diethyl phthalate (DEP) has been investigated in an undivided electrolysis device by electrochemical oxidation processes. Hydroxyl radical (HO[•]) was determined in the reaction mixture by the electron spin resonance spectrum (ESR). The result indicated that the Pd/C catalyst in Pd/C gas-diffusion electrode system accelerated the two-electron reduction of fed O₂ to H₂O₂, which is in favor of producing HO[•]. Additionally, the percentage removal of DEP and COD reached about 80.9 and 40.2% after 9 h electrolysis, respectively. It suggested that most of DEP were oxidized to intermediates using the Pd/C gas-diffusion electrode. Furthermore, the ratio of BOD₅/COD of resulted solutions was three times larger than the initial ones. Hence, the electrochemical oxidation enhanced the biodegradation character of the DEP solution. Finally, main aromatic intermediates (e.g., monoethyl phthalate (MEP) and phthalic acid (PA)) and main aliphatic carboxylic intermediates (e.g., formic, mesoxalic, oxalic, malonic, succinic, maleic, dodecanoic, and hexadecanoic acids) were identified by GC–MS. Moreover, a reaction scheme involving all these intermediates was proposed.

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1. Introduction

Phthalate esters (PAEs) are one kind of important industry products widely used. Commonly, PAEs are used primarily as plasticizers in the plastics, paint, and coating industry, and also in manufacture of insecticide carriers and propellants [1]. Owing to their widely production and utilization, PAEs are ubiquitous aqueous persistent organic pollutant in the environment. The United States Environmental Protection Agency (USEPA) and its international counterparts have classified PAEs as priority pollutants and as endocrine-disrupting compounds [2]. The short-chained phthalate esters, such as diethyl phthalate (DEP) are the most frequently found PAEs in diverse environmental samples including surface marine waters, freshwaters, and sediments, because of the discharge of wastewater and leaching and volatilization in the plastic manufacture and usage [3,4]. As the accumulation of PAEs in the environment has become a serious problem nowadays, it is very urgent to develop an effective method to remove and treat these contaminants. Traditional treatment processes, such as biological treatments are not effective for the degradation of PAEs [5–7].

Advanced oxidation processes (AOPs) have attracted much attention for their treatment of wastewater containing PAEs [8–11]. Especially, the electrochemical oxidation for the treatment of wastewater has been investigated, because of its ease of control, amenability to automation, high efficiency, and environmental compatibility [12]. Meanwhile, dimensionally stable anodes (DSA), which are typically prepared by thermal deposition of a thin layer of metal oxide (e.g., SnO₂, PbO₂, or IrO₂) on a support metal, have been widely used for the oxidation of aromatic pollutants [13–19]. Usually, the electrochemical treatment can mineralize organic pollutants by the strong oxidant, such as hydroxyl radicals (HO[•]) which is in situ generated by the electrochemical reaction on the electrode surface [20].

Very recently, indirect electro-oxidation methods for the wastewater treatment involving the H₂O₂ electrogeneration on the cathode have been developed. The cooperative oxidation of active anodes and electrogenerated oxidant species on the cathode is expected to increase notably the degradation rate of organic compound. The cathode material, such as carbon/polytetrafluoroethylene (C/PTFE) [21–24], graphite [25,26], carbon felt [27–30], and reticulated vitreous carbon [31,32] are used to electrogenerate H₂O₂ which left no hazardous residuals but oxygen and water after reaction with the organic compound. It has been reported that H₂O₂ can be electrochemically generated by reduction of dissolved oxygen in an acidic solution:



* Corresponding authors. Tel.: +86 10 62336615; fax: +86 10 62336596.
E-mail addresses: wanghui616@gmail.com (H. Wang), bzy@mail.ipc.ac.cn (Z.-Y. Bian).

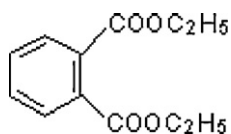


Fig. 1. Molecular structure of DEP.

The generation of H_2O_2 can be coupled with Fe^{2+} to produce hydroxyl radicals (OH^\bullet) which are strong enough to non-selectively oxidize most organic compounds. Therefore, the term of “electro-Fenton” is applied. However, the disadvantage of electro-Fenton process is the iron sludge formation [21–24,27–33].

In a well-designed electrochemical reactor, the organic compound degradation is expected to take place by anodic oxidation and H_2O_2 (electrogenerated on the cathode) oxidation synchronously. In present research, a self-made gas-diffusion electrode as the cathode and a $\text{Ti}/\text{IrO}_2/\text{RuO}_2$ anode were used for the electrochemical degradation of DEP (Fig. 1). On the basis of pollutant degradation by the anode, the cathode reaction was exploited to remove DEP and enhance the biotreatment character of the solution. Additionally, HO^\bullet was determined in the reaction mixture by the electron spin resonance spectrum (ESR). Finally, a degradation mechanism of DEP in the electrolysis device has also been investigated systematically.

2. Experimental

2.1. Preparation of Pd/C catalyst and gas-diffusion cathode

Pd/C catalysts with a Pd load of 0.5 wt% were prepared by the hydrogen gas reduction, and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). In the catalyst, Pd particles with an average diameter size of 4.1 nm were highly dispersed in the activated carbon with an amorphous structure; Pd content on the surface of the Pd/C catalyst reached 1.3 at% (atomic concentration). The Pd/C gas-diffusion cathodes were prepared according to the reported procedure (activated carbon powder instead of Pd/C catalyst in the C/PTFE gas-diffusion cathode) [34].

2.2. Procedures

Electrolysis was conducted in an undivided electrolysis device of 100 mL with a $\text{Ti}/\text{IrO}_2/\text{RuO}_2$ anode (16 cm^2) and a gas-diffusion cathode (16 cm^2). A schematic of the experimental setup is shown in Fig. 2. A laboratory direct current power supply with current-voltage monitor was employed to provide the electric power. The experimental conditions were as follows: the initial DEP concentration was 100 mg L^{-1} ; the current density was 39 mA cm^{-2} ; the concentration of supporting electrolyte (Na_2SO_4) was 0.05 mol L^{-1} ; the distance between electrodes was 2 cm; the initial pH was 7.0. Before starting electrolysis, air was fed for 5 min with a flow rate of 25 mL s^{-1} in order to keep the electrolysis solution oxygen saturated. Furthermore, air was sequentially fed into the electrolysis device till the end of electrolysis process.

2.3. Analytical methods

The radicals were determined by ESR measurements, which were performed in the X-band on a JES-FE3AX ESR spectrometer (JEOL, Tokyo, Japan) at room temperature. ESR spectrometer was set as follows: microwave frequency, 9.44 GHz; microwave power, 20 mW; modulation frequency, 100 kHz; modulation amplitude, 0.5 G; center field, 3367 G; scan width, 100 G; receiver gain, 2×10^3 ; time constant, 0.3 s; sweep time, 4 min. The ESR

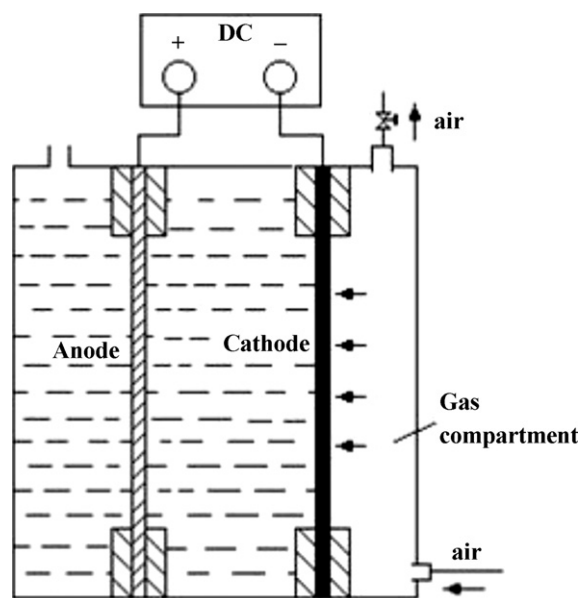


Fig. 2. Schematic diagram of the electrolysis apparatus.

spin trapping agent was 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, 11.1 mmol L^{-1}).

The H_2O_2 concentration accumulated during electrolysis was determined by the titration with permanganate using a standard procedure [32]. The SHIMADZU TU-1601 UV spectrometer was used to analyze the electrolyte in which spectral bandwidth was 0.2 nm and quick scanning rate was used. Sampling interval was 1.0 nm. Several other water quality parameters, such as BOD_5 and COD were measured according to the methods described in the Standard Methods for the Examination of Water and Wastewater [35].

DEP and stable organic intermediates were separated and identified by GC-MS using a ThermoFinnigan Trace DSQ consisting of an Rtx-5MS column ($15\text{ m} \times 0.25\text{ mm} \times 0.25\text{ mm}$) and a mass spectrometer operating in EI mode at 70 eV. To identify DEP by GC-MS, several solutions of 100 mg L^{-1} DEP in 0.05 mol L^{-1} Na_2SO_4 were electrolyzed for 2, 4, and 6 h. A 100 mL water sample was extracted with 10 mL of dichloromethane. After the second extraction of the water sample, the extracts were combined and dried on anhydrous sodium sulfate and concentrated to a few milliliters. A volume of $1\text{ }\mu\text{L}$ of this phase was directly analyzed by GC-MS using a Rtx-5MS column with a temperature ramp of $40\text{ }^\circ\text{C}$ for 1 min, $30\text{ }^\circ\text{C min}^{-1}$ up

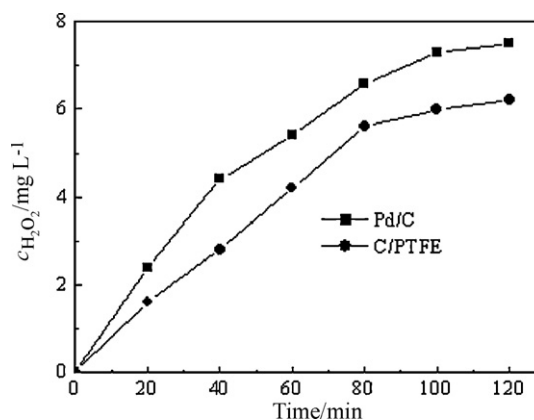


Fig. 3. Variation of accumulated H_2O_2 concentration with electrolysis time. Concentration of supporting electrolyte (Na_2SO_4): 0.05 mol L^{-1} ; current density: 39 mA cm^{-2} .

to 160 °C, 20 °C min⁻¹ up to 220 °C. The temperature for the injector and detector were 220 and 250 °C, respectively. High pure nitrogen was used as a carrier gas with a flow rate of 1.2 mL min⁻¹. Generated stable organic intermediates formed after electrochemical degradation treatment was also identified by GC–MS. The electrolyzed solution (5 mL) was lyophilized and the remaining solid was diluted with 2 mL of (1:1) *n*-butyl alcohol:hydrochloric acid under stirring and heating at 70 °C for 40 min. The resulting esterified derivatives thus obtained were detected and identified by GC–MS using the column with a temperature ramp of 40 °C for 2 min, 25 °C min⁻¹ up to 180 °C, hold 1 min, 25 °C min⁻¹ up to 220 °C and hold 10 min using high pure nitrogen as the carrier gas (flow rate 1.2 mL min⁻¹). The temperature of the injector and detector were 220 and 250 °C, respectively.

3. Results and discussion

3.1. Hydrogen peroxide and hydroxyl radical electrogenerated on the gas-diffusion electrode

In an undivided electrolysis device, the gas-diffusion cathode catalyzes the two-electron reduction of O₂ to H₂O₂ [36]. A titration method was used to detect H₂O₂ concentration accumulated in the undivided electrolysis device. Fig. 3 shows the change of H₂O₂ concentration with the electrolysis time in a 0.05 mol L⁻¹ Na₂SO₄ solution. With the electrolysis performs, the amount of H₂O₂ increased in these systems. After 120 min, the concentration of H₂O₂ reached to 6.2 mg L⁻¹ in the C/PTFE gas-diffusion electrode system, which was lower than the concentration of 7.5 mg L⁻¹ in the Pd/C gas-diffusion electrode system. It can be attributed to that Pd/C catalyst accelerates the two-electron reduction of O₂ to H₂O₂ on the cathode.

The Ti/IrO₂/RuO₂ anode which was typically prepared by thermal deposition of a thin layer of metal oxide on a support metal has been used for the oxidation of organic pollutants. The mechanism of the electrochemical degradation of organic compound on the metallic oxide Ti/IrO₂/RuO₂ anode is very complex and is not yet fully understood. However compared with the previous reports [37], a preliminary conclusion could be drawn about the mechanism of the electrochemical degradation of DEP in the present system. There are two oxidation pathways take place in the present system. One is anodic electrochemical oxidation process by MO_x(OH•) or MO_{x+1} produced on the anode surface are involved in the degradation of DEP on the anode [38]. The other is the cathodic HO• oxidation process in which the gas-diffusion cathode catalyzes the two-electron reduction of O₂ to H₂O₂, which may be converted

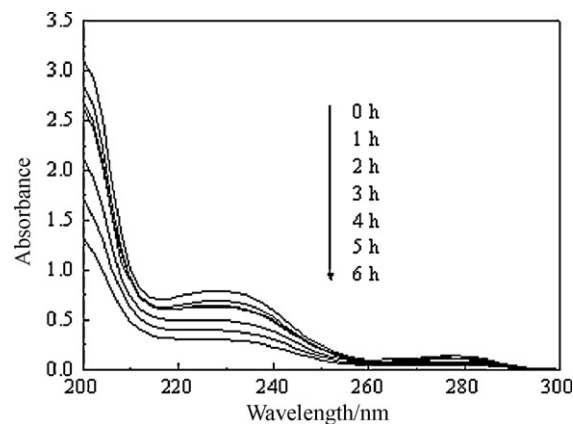
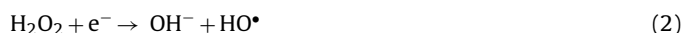


Fig. 5. The analysis of DEP by UV scanner at different electrolysis time. Concentration of DEP: 100 mg L⁻¹; concentration of supporting electrolyte (Na₂SO₄): 0.05 mol L⁻¹; current density: 39 mA cm⁻².

to HO• [39]:



ESR was used to quantitatively determine the free radical in the undivided electrolysis device. Fig. 4 shows the typical ESR spectrum obtained after 15 min electrolysis in the DMPO solution. The spectrum was composed of quartet lines with the peak height ratio of 1:2:2:1. The ESR parameters (hyperfine constants $a_N = a_H = 14.0$ G and g -value = 2.0065) coincided with those of DMPO-OH• adduct as demonstrated previously [40], confirming that the quartet signal is DMPO-OH• adduct. The adduct peak of the Pd/C catalyst modified electrode is higher than that of the no catalyst modified electrode (C/PTFE gas-diffusion electrode). This can be attributed to that the HO• concentration in the Pd/C gas-diffusion electrode system is higher than that of the C/PTFE gas-diffusion electrode system.

The concentrations of H₂O₂ and hydroxyl radical in the Pd/C gas-diffusion electrode system are higher than that of the C/PTFE gas-diffusion electrode system (see Figs. 3 and 4). It indicated that the Pd/C catalyst in Pd/C gas-diffusion electrode system accelerated the two-electron reduction of O₂ to H₂O₂ when feeding air, which is in favor of producing HO•. In the following experiments, the electrochemical degradation of DEP was investigated in an undivided electrolysis system, feeding with air, using the Pd/C gas-diffusion cathodes.

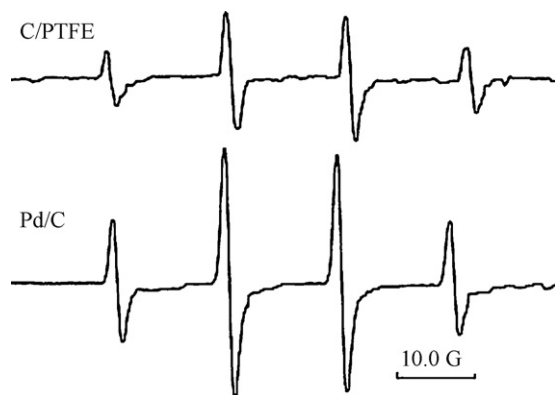


Fig. 4. ESR spectra of HO• radicals trapped by DMPO in the electrolysis device. Concentration of DMPO: 11.1 mmol L⁻¹; concentration of supporting electrolyte (Na₂SO₄): 0.05 mol L⁻¹; current density: 39 mA cm⁻².

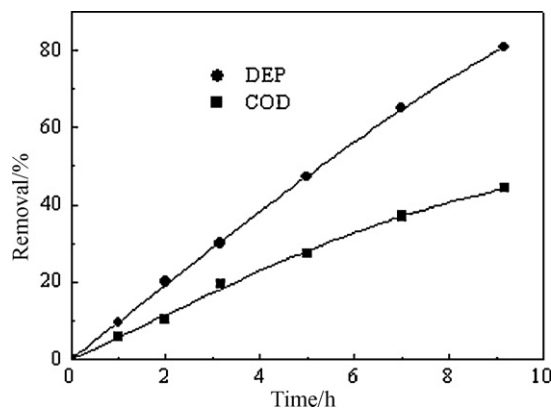


Fig. 6. Change of DEP and COD removal with electrolysis time. Concentration of DEP: 100 mg L⁻¹; concentration of supporting electrolyte (Na₂SO₄): 0.05 mol L⁻¹; current density: 39 mA cm⁻².

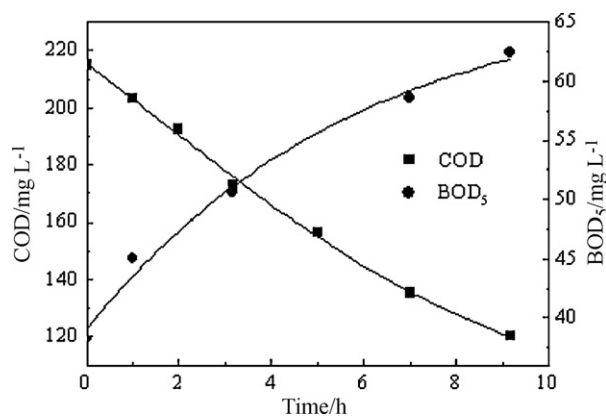


Fig. 7. Change of the value for COD and BOD₅ during electrochemical oxidation. Concentration of DEP: 100 mg L⁻¹; concentration of supporting electrolyte (Na₂SO₄): 0.05 mol L⁻¹; current density: 39 mA cm⁻².

3.2. Removal of DEP

The changes of UV absorption spectrum of DEP with electrolysis time (0, 1, 2, 3, 4, 5, and 6 h) are shown in Fig. 5. DEP shows two significant and characterized UV absorption bands at 227 and 277 nm [1,8]. The absorption intensity of DEP decreased with the electrolysis time. Finally, there were no obvious absorption peaks after 6 h electrolysis. It indicated that concentration of DEP in the Pd/C gas-diffusion electrode system decreased with prolonging the electrolysis time. The degradation of DEP was attributed to the cooperatively oxidation processes include electrochemical oxida-

tion at the anode and H₂O₂ and HO• produced by the reduction of oxygen at the cathode.

Fig. 6 shows the percentage removal of DEP and COD with electrolysis time in the Pd/C gas-diffusion electrode system. The percentage removal of DEP increased from 9.5 to 80.9% when electrolysis time was extended from 1 to 9 h. However, the percentage removal of COD varied from 5.6 to 40.2% during the same period. Hence, the change of the COD removal was not exactly fit to that of the DEP removal. This indicated that most of DEP were oxidized to intermediates, which were not be further oxidized to CO₂ and H₂O.

Fig. 7 describes the changes of COD and BOD₅ during DEP electrochemical oxidation. The initial value of BOD₅ of DEP solution was below 39 mg L⁻¹, and the initial value of COD was 215 mg L⁻¹.

Table 1
Intermediates identified in the DEP solution during electrochemical oxidation.

Number	Intermediates	Molecular formula	Retention time/min
1	Formic acid	HCOOH	4.45
2	Mesoxalic acid	$\text{HOOC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{COOH}$	4.91
3	Oxalic acid	$\begin{array}{c} \text{COOH} \\ \\ \text{COOH} \end{array}$	6.29
4	Malonic acid	$\begin{array}{c} \text{COOH} \\ \\ \text{C} \\ \\ \text{COOH} \end{array}$	6.70
5	Succinic acid	$\begin{array}{c} \text{C}-\text{COOH} \\ \\ \text{C}-\text{COOH} \end{array}$	7.29
6	Maleic acid	$\begin{array}{c} \text{COOH} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{COOH} \end{array}$	7.39
7	Dodecanoic acid	CH ₃ (CH ₂) ₁₀ COOH	8.53
8	Phthalic acid (PA)		9.67
9	Hexadecanoic acid	CH ₃ (CH ₂) ₁₄ COOH	10.80
10	Monoethyl phthalate (MEP)		11.37

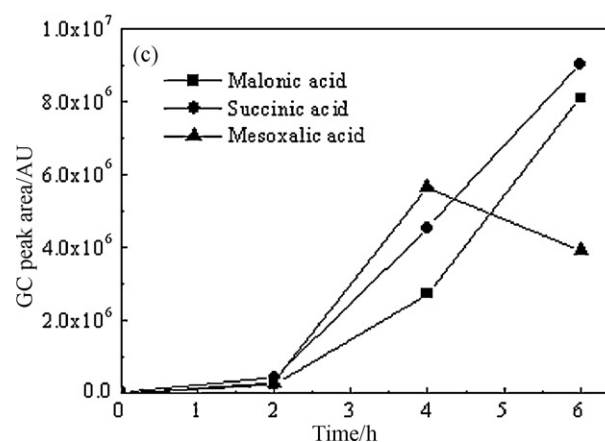
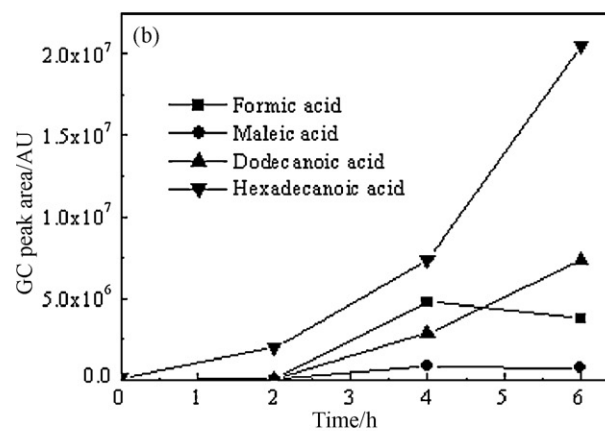
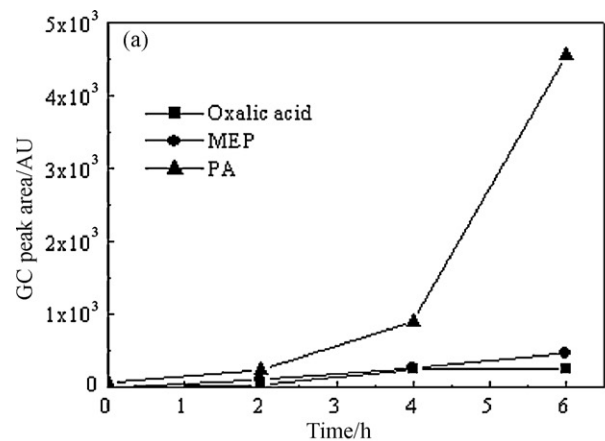


Fig. 8. Change of intermediates concentration during electrochemical oxidation of DEP. Concentration of DEP: 100 mg L⁻¹; concentration of supporting electrolyte (Na₂SO₄): 0.05 mol L⁻¹; current density: 39 mA cm⁻².

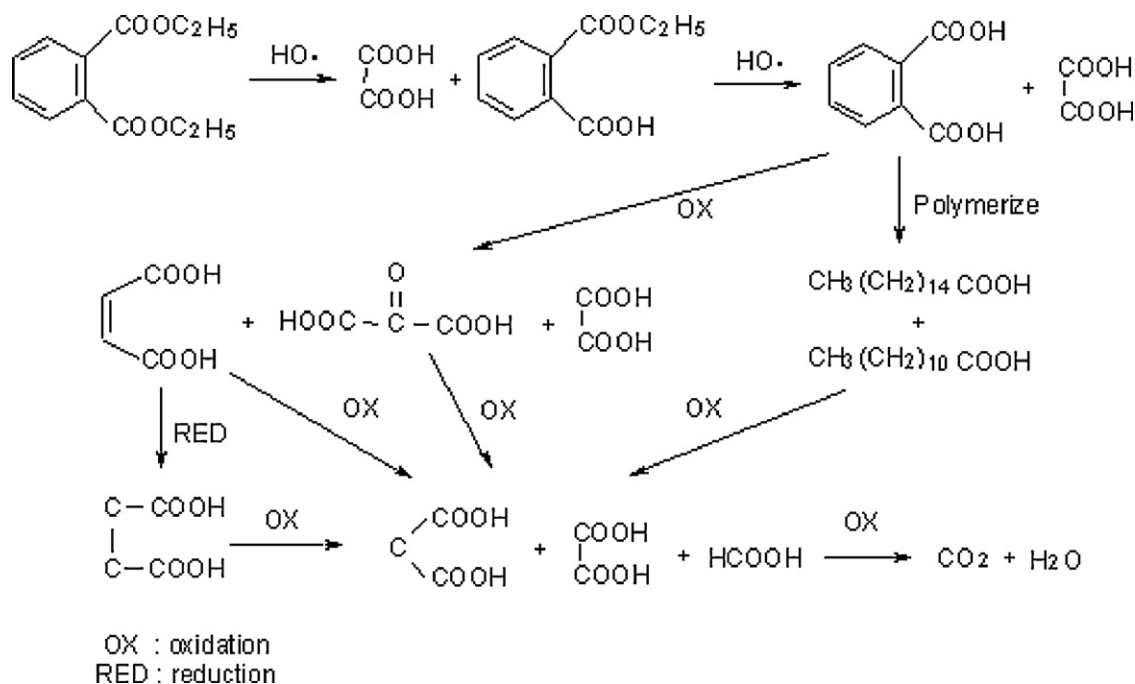


Fig. 9. Reaction pathway for the electrochemical oxidation of DEP.

Hence, the ratio of BOD₅ to COD was only 0.18, which indicated the solution of DEP was non-biodegradation and toxic to microbiological in a municipal sewage plant. During the electrochemical oxidation, the ratio of BOD₅/COD increased sharply from 0.18 to 0.52. After 9 h electrolysis, the ratio of BOD₅/COD of the initial solution was three times larger than the initial one. Therefore, the electrochemical oxidation can enhance the biodegradation character of the DEP solution.

3.3. Identification of intermediates and their evolution

An attempt was made to identify the intermediates formed in the electrocatalytic degradation of DEP using GC–MS. The nature of intermediates was investigated by degrading a 100 mg L⁻¹ DEP solution of pH 7.0 at 39 mA cm⁻² in an undivided electrolysis device for 2, 4, and 6 h. The products were identified based on their molecular ion and mass spectrometric fragmentation peaks compared with the chemical standards. The gas chromatogram of organic compound collected exhibited the peak of the initial DEP at $t_r = 14.57$ min, along with another 10 peaks which were identified by mass spectrometry and ascribed to formic, mesoxalic, oxalic, malonic, succinic, maleic, dodecanoic, phthalic acid (PA), hexadecanoic acids, and monoethyl phthalate (MEP) (Table 1). Fig. 8 shows the evolution of aromatic intermediates and carboxylic acids during the degradation of DEP by the Pd/C gas-diffusion electrode system. Therefore, considered the previous reports [41,42] and the analytic results of GC–MS, the formation and destruction of main intermediates can be observed.

As shown in Fig. 8, the main aromatic compounds are MEP and PA. The main aliphatic intermediates are aliphatic carboxylic acids, such as formic, mesoxalic, oxalic, malonic, succinic, maleic, dodecanoic, and hexadecanoic acids. The maximum concentration of formic, mesoxalic, maleic, and oxalic acids present at 4 h, and then decrease quickly. After 6 h, most of aliphatic carboxylic acids were transformed into carbon dioxide and water. These results indicated that in the Pd/C gas-diffusion electrode system aromatic intermediates were transformed into carboxylic acids, because they reacted rapidly with the large amount of HO• formed from the anode and cathode, which Pd/C gas-diffusion electrode catalyzes the two-

electron reduction of O₂ to H₂O₂, and then H₂O₂ may favorable be converted to HO•.

Fig. 9 presents a degradation pathway of DEP in the undivided electrolysis device by the Pd/C gas-diffusion cathode system. It was deduced that the electrocatalytic degradation of DEP mainly occurred via the aliphatic chain cracked rather than the aromatic ring decomposition firstly. Muneer et al. [41] also reported that in the photocatalytic degradation of DEP in aqueous suspensions of titanium dioxide, PA was detected as one of intermediate products. It was believed that either ethyl or ester chain scissions of the aliphatic part of DEP was the dominant degradation mechanism of the process [1], with the aromatic ring remaining intact. Cartwright et al. [42] identified MEP and PA as the only products in the degradation of DEP. The detection of MEP and PA during the electrochemical degradation of DEP was consistent with these reports and the degradation pathway described there. Primary degradation of DEP to PA had been reported [42] to involve the hydrolysis of two diethyl chains of the phthalate to produce the monoester monoethyl phthalate (MEP) and then PA. Therefore, based on the present experimental data and literature reports, the electrochemical degradation pathway of DEP in the aqueous solution is illustrated in Fig. 9. The degradation pathway was proposed as follows: the pathway of DEP degradation involved the sequential oxidation breakage of both ester groups of the phthalate, forming the monoester (MEP) and then PA (through removal of the second ethyl group). The continually oxidation of PA, after ring opening, then led to the formation of aliphatic carboxylic acids, such as maleic, mesoxalic, and oxalic acids, which were degradation to malonic acid, and further formed formic acid. Whereas, HO• attacked on PA, after ring opening, led to the formation of aliphatic carboxylic acids, which polymerized to long-chained aliphatic carboxylic acids, such as dodecanoic and hexadecanoic acids, and further formed mesoxalic, and oxalic acids. The parallel reduction of maleic acid on the cathode, led to the formation of succinic acid. Finally, the terminal products were carbon dioxide and water. Owing to the low current efficiency of the electrochemical treatment, in practical use, it was not necessary to degrade DEP to the final products, CO₂ and H₂O. It may be more worthwhile to degrade DEP to the biodegradable stage-aliphatic carboxylic

acids which could then be economical treated by the biological process.

4. Conclusions

The electrochemical degradation of DEP was studied in an undivided electrolysis device with a Ti/IrO₂/RuO₂ anode and a gas-diffusion cathode. The cathode generated H₂O₂ through two-electron reduction of fed molecule oxygen in the electrolysis. At the same time, HO• was determined in the electrochemical systems by ESR. The concentrations of H₂O₂ and HO• used the Pd/C gas-diffusion cathode were higher than that of the C/PTFE one. It indicated that the Pd/C catalyst in Pd/C gas-diffusion electrode system accelerates two-electron reduction of O₂ to H₂O₂ which is in favor of producing HO•. Meanwhile, the percentage removal of DEP and COD reached 80.9 and 40.2% after 9 h of electrolysis, respectively, which suggested that most of DEP was oxidized to intermediates using the Pd/C gas-diffusion electrode. Furthermore, the ratio of BOD₅/COD of the DEP solution was three times larger than the initial one. The electrochemical oxidation enhanced the biodegradation character of the DEP solution. Hence, the degradation of DEP was attributed to the cooperatively oxidation processes include electrochemical oxidation at the anode and H₂O₂ and HO• produced by the reduction of oxygen at the cathode. Furthermore, the electrolysis products determined by GC–MS indicated that the main aromatic intermediates were MEP and PA. Whereas, the main aliphatic intermediates were aliphatic carboxylic acids, such as formic, mesoxalic, oxalic, malonic, succinic, maleic, dodecanoic, and hexadecanoic acids. The analysis of the intermediate products formed during the electrochemical degradation provided useful information on the degradation pathways.

Acknowledgements

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